A Systematic Analysis of Potassium, Rubidium and Cesium and its Application to Sea-Muds

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In order to determine the amount of each component in a mixture of potassium, rubidium and cesium, systematic methods have been established by combining methods for the separation and determination of these elements which have already been examined. Having been confirmed to be satisfactory for this purpose, the methods have been applied for an analysis of sea-muds.

INTRODUCTION

There have been several methods reported for the determination of potassium, rubidium and cesium in their mixtures. However all the chemical reactions used in these methods are not specific, or selective, and therefore the exact separation and determination of each component is difficult. However, the systematic methods reported here made use of the specific or the selective reaction with one or two among these elements and therefore the method is more reliable than any of the conventional methods. As a matter of fact, the specific or selective reaction is indispensable for the exact determination of potassium, rubidium and cesium because their chemical behaviors are extremely similar. Each part of these systematic methods has already been reported in detail. Various kinds of mixtures containing known amounts of potassium, rubidium and cesium have been analyzed by these systematic methods and the results obtained have been found to be satisfactory. Then the method was applied to the determination of these elements in sea-muds.

EXPERIMENT

1) Reagent and Apparatus

The same as those in the previous reports was used.

2) Procedure

The principle of the procedure is based on the fact that the separation of rubidium and cesium from potassium is made selectively by the $Na_2AgBi(NO_2)_6$ reagent and the separation and determination of cesium is made by the $KBiI_4$ or the $NaBiI_4$ reagent. However, in order to simplify the procedure, the indirect

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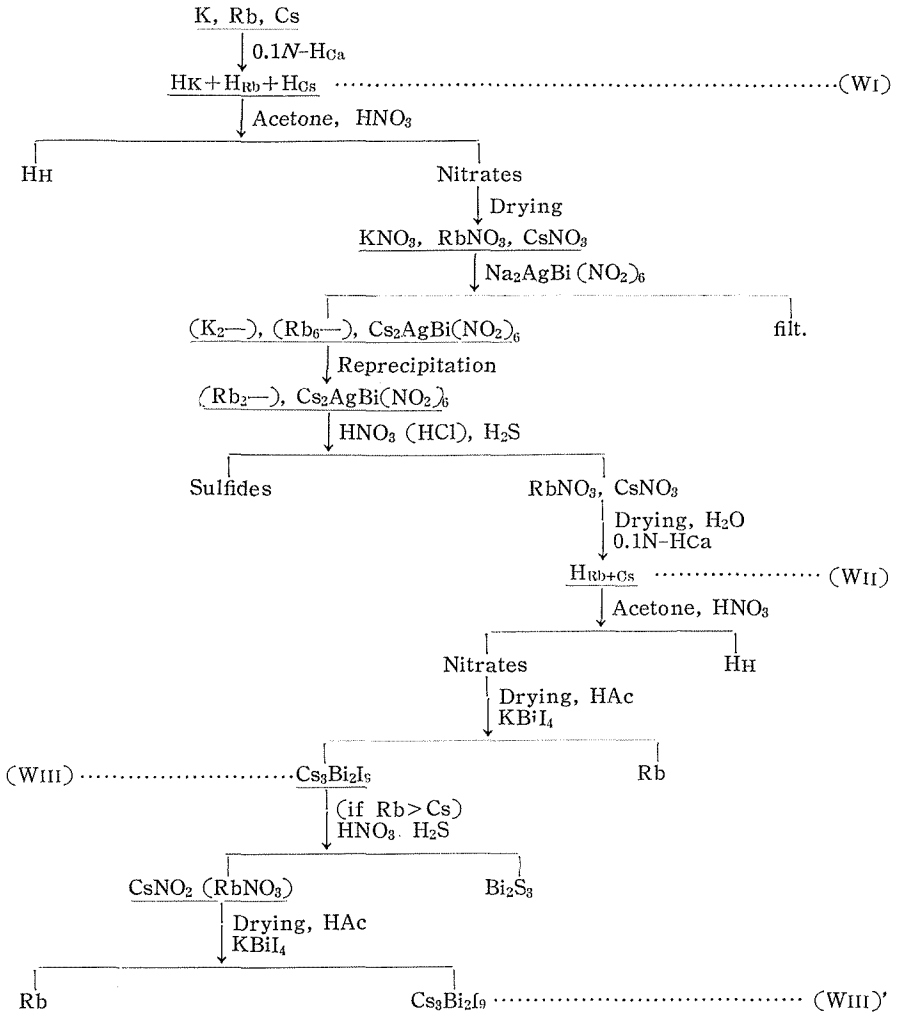
methods as described later were adopted and the two typical methods among them, that is to say, procedures (A) and (B), were chosen in accordance with the kind of sample which seemed to be most frequently encountered. Procedure (A) is appropriate for a sample in which potassium, rubidium and cesium are present in nearly the same amount, but procedure (B) is appropriate for samples in which the amounts of potassium, rubidium and cesium decrease in order of cesium from potassium.

Procedure (A). As the details of each step of the procedure have already been reported, their outline is shown in Table 1. The principle of the method is as follows :

Table 1.

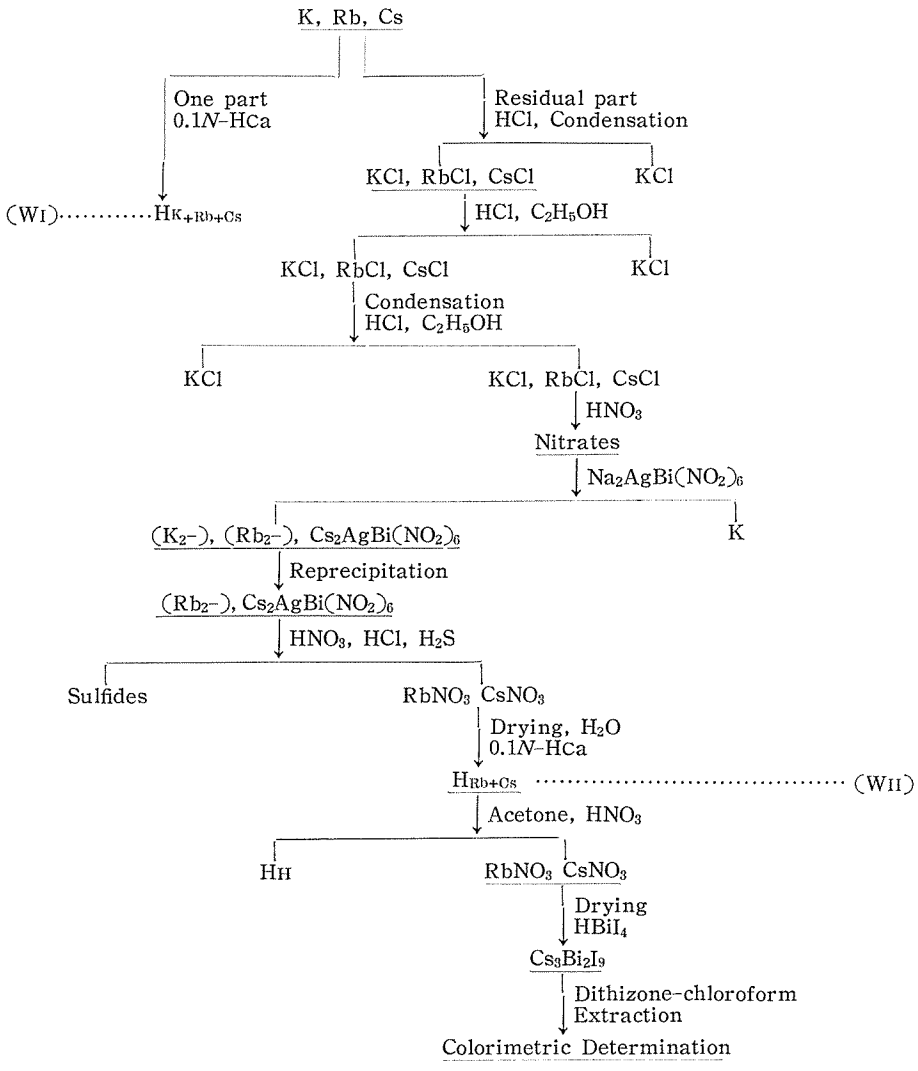


For a mixed sample of potassium, rubidium and cesium, the weight of their dipicrylaminates (W_I) is found. After removal of the potassium, the weight of the residual dipicrylaminates (W_{II}) is found. Then the amount of cesium is

found from the weight of $Cs_3Bi_2I_9$ (W_{III}), or $(W_{III})'$ if the amount of rubidium in the sample is larger than that of cesium. Thus the amount of potassium dipicrylaminate (H_K) is found as the difference of (W_I) and (W_{II}). The amount of cesium found by $Cs_3Bi_2I_9$ is converted into H_{Cs} and then the amount of rubidium dipicrylaminate is found as the difference of (W_{II}) and H_{Cs}. Therefore the amounts of potassium, rubidium and cesium can all be obtained by such an indirect method.

Procedure (B). The outline of the procedure is shown in Table 2. The principle of the method is as follows :

Table 2.



For a definite part of a sample containing potassium, rubidium and cesium, the sum of their dipicrylaminates (W_I) is found and then the sum of their dipicrylaminates in the original sample is found. After removal of the potassium,

the sum of the dipicrylaminates of rubidium and cesium (W_{II}) is found and therefore the sum of their dipicrylaminates in the original sample is found. As for the mixture of rubidium and cesium, tne amount of cesium is determined by tne indirect colorimetric method. In this case, the amount of $H_{K+Rb+Cs}$ is nearly equal to that of H_K and the amount of H_{Rb+Cs} is nearly equal to that of H_{Rb}. Almost all of the samples produced from nature can be analysed by this method. Procedures for analysis of samples other than the above mentioned ones were neglected because they could be easily devised by a little modification of the previous procedure and moreover such samples would seldom be met with.

EXPERIMENTAL RESULTS

The results obtained by procedure (A) are shown in Table 3. As seen from the table, the amount of each component in the mixture of potassium, rubidium and cesium can be almost satisfactorily determined. However, it is rather difficult to separate rubidium and cesium from potassium. Then the results obtain-

Table 3. Systematic analysis of the mixtures of K, Rb and Cs.

Exp. No.	1	2	3	4	5	6	7	8
K taken (mg.)	4.99	9.99	4.99	9.99	19.98	19.98	4.99	9.99
Rb taken (mg.)	5.08	5.08	5.08	2.54	5.08	2.54	1.02	2.54
Cs taken (mg.)	10.15	5.08	10.15	2.54	5.08	2.54	1.02	1.02
W_I (mg.)	135.30	173.70	134.80	148.80	294.60	269.90	71.30	141.30
H_K (mg.)	59.50	120.45	60.25	120.69	241.72	242.36	60.04	120.51
K (mg.)	4.88	9.87	4.94	9.89	19.81	19.86	4.92	9.87
W_{II} (mg.)	75.80	53.25	74.55	28.11	52.88	27.54	11.26	20.79
H_{Rb} (mg.)	32.52	31.83	30.67	16.82	31.20	16.33	6.54	16.28
Rb (mg.)	5.31	5.20	5.00	2.75	5.09	2.67	1.07	2.66
W_{III}' (mg.)	49.52	24.52	50.22	12.92	24.82	12.82	5.42	5.14
Cs (mg.)	10.08	4.99	10.22	2.63	5.05	2.61	1.10	1.05
H_{Cs} (mg.)	43.28	21.42	43.88	11.29	21.68	11.21	4.72	4.51

Table 4. Systematic Analysis of the mixture of K, Rb and Cs.

Exp. No			2	1	3	4	5	6
Sample	K	(g.)	1.000	2.000	4.000	10.000	0 500	0.200
	Rb	(mg.)	2.00	5.00	10.00	20.00	2.00	1.00
	Cs	(μg.)	20	50	100	200	15	10
K (g.)	Found		1.004	1.978	3.998	10.034	0.501	0.200
	Error		+0.004	−0.022	−0.002	+0.034	+0.001	±0.000
H_{Rb+Cs}		(mg.)	12.67	31.42	56.53	126.40	11.86	7.13
Rb (mg.)	Found		2.07	5.13	9.23	20.63	1.94	1.16
	Error		+0.07	+0.13	−0.77	+0.63	−0.06	+0.16
Cs (μg.)	Found		23	46	92	184	17	12
	Error		+3	−4	−8	−16	+2	+2

ed by procedure (B) are shown in Table 4. It is seen from the table that the amount of each component in such a sample, in which the ratio among potassium, rubidium and cesium is extremely different, can be exactly determined.

ANALYSIS OF SEA-MUDS

(a) **Sample.** In relation to their fertilizability, such sea-muds as shown in Table 5 were used as samples for analysis of potassium, rubidium and cesium.

Table 5. Samples for analysis.

Sample	Appearance	Sampling place
A	Muddy	Futago-shima, Kure-ko-nai, Hiroshima Pref.
B	Muddy	Futago-shima, Kure-ko-nai, Hiroshima Pref.
C	Sandy	Noti Kozaki-cho, Toyoda-gun, Hiroshima Pref.
D	Sandy	Mino-shima, Kawaguchi-mura, Ashina-gun, Hiroshima Pref.
E	Muddy	Nishio-shima, Oshima-mura, Asaguchi-gun, Okayama Pref.
F	Sandy	Takamatu, No.2088, Shizuoka-shi

(b) **Preliminary experiment.** In order to estimate a small amount of cesium in a solid sample as accurately as possible, the following preliminary experiment was made with regard to the above samples.

Five grams of a sample which had been passed through a 100 mesh sieve was taken in a 100 ml. of porcelain dish and to it 10 ml. of water and 1 μC of Cs-137 were added. Then the suspension was vaporized to dryness, 10 ml. of water was again added and it was heated for some time. Then the contents were filtered through a glass-filter and the residue was washed several times with hot water. The filtrate was vaporized to dryness and the activity of each residue was separately measured. A very strong activity was found in the insoluble residue, but no activity was found in the residue from the filtrate. It was also found that the activity in the insoluble residue was not removed even with treatment with dilute hydrochloric acid.

The following study was also made. Most of the above sample which was vaporized to dryness with 1 μC of Cs-137 was removed with a spoon, and the residual part of it is removed as completely as possible by stirring with several parts of one gram of calcium carbonate. The activity of the porcelain dish was measured, but it was not in the least active.

From these experimental results, it is concluded that the exact recovery of a small amount of cesium in a solid sample ought to be obtained by the following procedure. A definite amount of Cs-137 is added to a definite amount of solid sample and after vaporizing to dryness, the sample is treated by the Lawrence-Smith Method.

(c) **Procedure.** Each sample which passed a 100 mesh sieve is dried at 105°~110°C for four hours and then 15 grams are taken in a 100 ml. of porcelain dish. 10 ml. of water and 2 μC of Cs-137 are added, and it is vaporized to dry-

ness on a steam-bath. One gram is decomposed by the Lawrence-Smith Method, and all the alkali elements are extracted with hot water. To the extracted solution, ammonium hydroxide aed ammonium carbonate are added to precipitate the calcium dissolved in the solution. The precipitate is filtered off and the filtrate is brought to 250 ml. with water after being concentrated. A definite volume of the solution is taken into a platinum crucible, vaporized to dryness, and the residue is ignited to drive off the accompanying ammonium salts. From the residual chlorides, the sum of the dipicrylaminates of potassium, rubidium and cesium is found. The other part of the solution is similarly treated, and the alkali chlorides are obtained. Then the dipicrylaminates of potassium, rubidium and cesium are produced, and they are processed in accordance with procedure (B).

(d) Results. The results obtained by this method are shown in Table 6. It

Table 6. Analysis of sea-muds.

Sample	Kind	A	B	C	D	E	F
	Weight (g.)	15.00	15.00	15.00	15.00	15.00	15.00
K_2O	(mg.)	366.7	238.5	540.0	666.0	438.7	243.0
K_2O	(%)	2.44	1.59	3.60	4.44	2.93	1.62
Rb_2O	(mg.)	5.03	5.83	4.34	4.95	3.14	2.65
Rb_2O	(%)	0.033	0.039	0.029	0.032	0.021	0.017
Cs Recooery	(%)	78.4	70.7	73.0	70.2	72.4	76.3
Cs_2O	(μg.)	116	148	101	122	93	78
Cs_2O	(%)	7.7×10^{-4}	9.8×10^{-4}	6.7×10^{-4}	8.1×10^{-4}	6.2×10^{-4}	5.2×10^{-4}

is seen from the table that the values of potassium, rubidium and cesium are considerably similar to Clarke's Number.

SUMMARY

Systematic methods for the determination, of potassium, rubidium and cesium have been established based on a selective or specific reaction with one or two among them. These methods were also found to be satisfactory for analysis of such samples as those commonly encountered. The mehtod was applied for an analysis of several kinds of sea-muds.